Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 16 (2012) 1206 – 1210

Energy Procedia

2012 International Conference on Future Energy, Environment, and Materials

Preparation of Self-organized Titania Nanotubes Electrode and Its Electrochemical Properties

Xiuqin CHEN[a]*, Xuping CHEN[b], Jie TANG[a], Shangfei CHEN[a]

[a]*Department of Urban Construction Engineering, Zhejiang College of Construction, Hangzhou 311231, China*
[b]*Department of Economic management, Zhejiang College of Construction, Hangzhou 311231, China*

Abstract

A new type TiO_2 electrode was fabricated by forming nanotube-like TiO_2 film on a Ti sheet in an anodic oxidation process. The micro-morphology and phase structure of it were analyzed by FE-SEM and XRD, respectively. The average diameters of these nanotubes rang from 80 to 150 nm. The evidences from the electrochemical station indicated that the TiO_2 nanotubes electrode had higher oxygen-librating potential than the conventional TiO_2 film electrode. And the experiments of photoelectrocatalytic degradation of 4-chlorophenol (4-CP) with this TiO_2-NTs array electrode as working electrode were carried out.

Keywords: Nanotubes electrode; TiO_2, anodic oxidation; oxygen-librating potential; 4-chlorophenol;

1. Intorduction

In recent years, TiO_2 nanotubes began to attract wide attention because of its novel larger surface area. TiO_2 nanotubes, in powder forms, have fabricated by templates synthesis[1] and hydrothermal chemical process[2]. For being no supported, they cannot be used as working electrodes in photoelectrocatalytic degradation of pollutants. Anodic oxidation processes were effective for the growth of titania nanotubes arrays on a pure Ti sheet[3-5]. And few reports have been found so far regarding the electrochemical properties and photoelectrocatalytic degradation of pollutants of this kind of TiO_2 nanotubes electrode.

* Corresponding author. Tel: 86-0571-82873761
Email address: chenxq73@126.com

 doi:10.1016/j.egypro.2012.01.192

In this paper, self-organized TiO_2 nanotubes electrodes were successfully grown by forming tube-like TiO_2 film on a Ti sheet in anodization processes. The micro-morphology and its oxygen-librating potentials were measured.

2. Materials and Methods

2.1. Materials

Titanium sheets (99.60% purity) were purchased from Baoye Titanium-nickel Industry Co., LTD. China. HF, HNO_3, H_2SO_4 acid, and acetone were of analytical grade.

2.2. Methods

Prior to treatment, Ti sheets ($10 \times 20 \times 0.5$ mm) were successively chemically etched in an acid mixture, ultrasonically cleaned in acetone solution, rinsed with deionized water (DI), and then dried in air at room temperature. The anodization was conducted in a two-electrode electro-chemical cell with a nickel gauze as cathode at a constant potential with magnetic agitation. The electrolyte consisted of 1 mol/L H_2SO_4 and little amount HF in water. After anodizing for two hours, the product was annealed at 400℃ for 40 min.

The electrochemical performance of the TiO_2 nanotubes electrodes, after annealed at 400℃ for 40 min, was tested by electrochemical station (CHI600B, Chenghua, China). The electrochemical cell used was a conventional three-electrode configuration with platinum thread and a saturate calomel electrode (SCE) as the counter electrode and reference electrode, respectively. Experiments were carried out in 0.2 mol/L H_2SO_4 at room temperature, with 1cm^2 of the sample surface exposed to the electrolyte.

The photoelectrocatalytic experiment was carried out under the following conditions: under visible-light irradiation (a 300 W Xe lamp, I_0 = 0.6 mW/cm^2) with any irradiation below 400 nm removed by 2 mol/L $NaNO_2$ solution, and 0.1 mol/L Na_2SO_4 as electrolyte. 1.5 V anodic bias potential was applied. The concentration of 4-chlorophenol (4-CP) was monitored by an HPLC. The tested nanotube film was calcined at 400℃ in air for 2 h. All values of the electrode potentials are referred to SCE in these experiments.

3. Results and Discussion

3.1. SEM analysis

Fig. 1 shows the FE-SEM images of the TiO_2 nanotubes electrodes (TiO_2-NTs electrodes), fabricated at different anodic potentials. Generally consideration, the self-organized TiO_2-NTs arrays are formed as a result of the competition between the field-enhanced formation of TiO_2 at the TiO_2/Ti interface and the field-enhanced dissolution of TiO_2, forming dissoluble $[TiF_6]^{2-}$ at the solution/TiO_2 interface[3-6]. When the anodic voltage is 10 V, the field-enhanced dissolution rate of TiO_2 was slow due to lower applied potential and only a few pits can be seen on the surface. Under the anodic voltage of 30 V, the field-enhanced dissolution rate of TiO_2 was much faster, which prevented nanotubes' formation, and only a highly disturbed porous structure was obtained. While at the potential ranging from 15 to 25 V, uniformed nanotubes arrays can be obtained[7]. The TiO_2-NTs are well-aligned and organized into high-density uniform arrays, oriented perpendicularly to the substrate. The average outer diameters of these tubes rang from 80 to 150 nm, with a large density of nearly 3×10^{13} cm^{-2}.

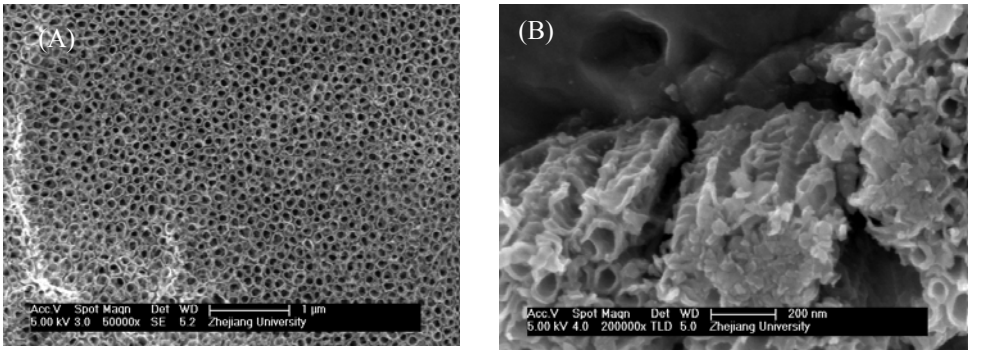

Fig.1 FE-SEM images of TiO_2-NTs arrays anodized under 25 V. (a) top view ; (b) cross section.

3.2. XRD analysis

XRD analysis shows that the as-anodized nanotubes were amorphous, while after annealed at 400℃ in air for 40 min, the anatase phase corresponding to 25.3º had been the majority, with little amount rutile phase appeared.

3.3. Oxygen-librating potential

Fig. 2 shows the polarizing curves of the TiO_2 electrodes fabricated at different potentials. The oxygen-librating potentials (U) of the electrodes are in turn of $U_{25\ V} > U_{15.7\ V} > U_{20\ V}$, respectively. Compared with that of the TiO_2 film electrode prepared by MOCVD, $U_{25\ V}$ is 0.3 V higher, see in Table 1. It means that oxygen librates more difficultly on the TiO_2-NTs array electrode than on the TiO_2 film electrode. At the same time, the opportunity of the pollutant being directly degraded on the surface of the nanotubes electrode is much higher. It means that the TiO_2-NTs electrode has the higher catalytic capability.

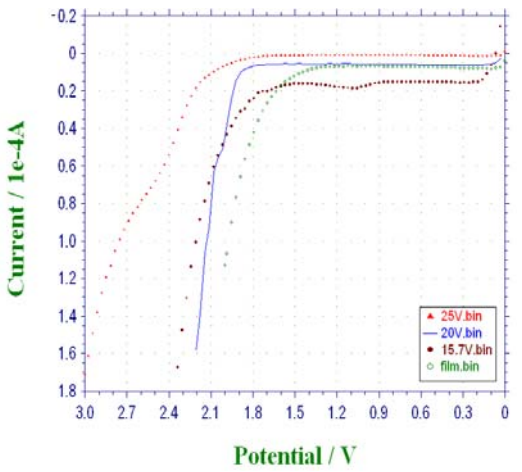

Fig.2 The polarizing curves of self-organized TiO_2-NTs arrays electrodes fabricated at different anodic potentials. Film means TiO_2 film electrode made by MOCVD.

Table 1 The contrast of the oxygen-librating potentials (OLP) of self-organized TiO_2-NTs arrays electrodes.

	TiO_2-NTs electrodes made under different anodic potentials (V)			Film electrode
	15.7	20.0	25.0	
OLP (V)	1.85	1.75	2.15	1.85

3.4. Photoelectrocatalytic performance

To further confirm their catalytic capability, the photoelectroncatalytic (PEC) degradation was performed in a conventional three-electrode configuration with the sample (25 V) served as the photoelectrocatalytic electrode, with 1 cm^2 effective area. The degradations of 4-CP in the photocatalysis (PC), electrocatalysis (EC) and photoelectroncatalytic (PEC) processes are varied. The degradation of 4-CP in PEC process had a 20% higher than that in PC process at 20 min, and 18% higher at 30 min (see in Fig. 3). The degradation of 4-CP in PEC process had a 55% higher than that in EC process at 20 min, and 58% higher at 30 min. It is possible that the recombination of photogenerated hole/electron pairs was suppressed by the external electric field. The more photogenerated holes/electron pairs remained, the higher rate 4-CP was decomposed.

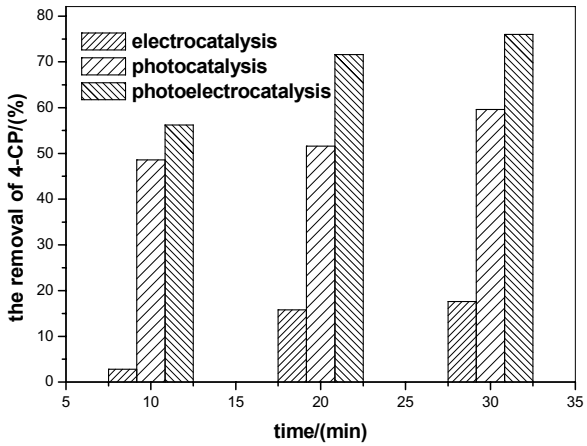

Fig. 3 The electrocatalysis, photocatalysis and photoelectrocatalysis processes of 4-CP solution of self-organized TiO_2-NTs arrays electrodes.

4. Conclusion

In summary, highly ordered TiO_2-NTs array electrode were fabricated on pure Ti sheets bu anodization process. The obtained TiO_2-NTs are well-aligned and organized into high-density uniform arrays, oriented perpendicularly to the substrate. The average outer diameters of these tubes rang from 80 to 150 nm. XRD analysis shows that the as-anodized nanotubes were amorphous, while after annealed at 400℃ in air for 40 min, the anatase and rutile phase appeared. Evidences obtained from electrochemical station indicated that the TiO_2-NTs array electrode had higher catalytic capability than TiO_2 film electrode. The oxygen-librating potentials (U) of the TiO_2-NTs electrode anodized at 25 U is 0.3 V higher than that of the TiO_2

film electrode prepared by MOCVD. The degradation of 4-CP in the photoelectrocatalytic processes is 75% after 30 min visible light irradiation.

Acknowledgements

The authors would like to acknowledge financial support for this work provided by the Undergraduate Technological Innovation Program of Zhejiang Province, China (Grant No. 2010R442005)

References

[1] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, Formation of titanium oxide nanotube. *Langmuir,* 1998, 14(11), 3160-3162.

[2] H. Tokudome, and M. Miyauchi, Electrochromism of titania-based nanotubes. Angew. *Chem. Int. Ed.,* 2005, 44(7), 1974-1977.

[3] D. Gong, C. A. Grimes, O. K. Varghese, W. C. Hu, R. S. Singh, Z. Chen, and C. D. Elizabrth, Titanium oxide nanotube arrays prepared by anodic oxidation. *J. Mater. Res.,* 2001, 16(12), 3331-3334.

[4] O. K. Varghese, D. Gong, M. Paulose, C. A. Grimes, and E. C. Dickey, Crystallization and high-temperature structural stability of titanium oxide nanotube arrays. *J. Mater. Res.,* 2003, 18(1), 156-165.

[5] Q. Cai, M. Paulose, O. K. Varghese, and C. A. Grimes, The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation. *J. Mater. Res.,* 2005, 20(1), 230-235.

[6] X. Quan, S. G. Yang, X. L. Ruan, and H. M. Zhao, Preparation of titania nanotubes and their environmental applications as electrode. *Environ. Sci. & Technol.,* 2005, 39(10): 3770-3775.

[7] X. Chen, X. Zhang, L. Lei, Fabrication and formation mechanism of self-organized TiO_2 nanotube arrays. *The Chinese journal of nonferrous metals*. 2010, 20 (9):1724-1731.